HOMOGENEOUS METALLOCENE ZIEGLER-NATTA CATALYSTS FOR THE OLEFINIMERIZATION OF OLEFIN IN ALIPHATIC HYDROCARBON SOLVENTS

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References Cited
U.S. PATENT DOCUMENTS
4,234,752 A 11/1980 Wu et al.
4,260,845 A 4/1981 Shioyama
4,473,444 A 9/1984 Feldman et al.
5,158,992 A 10/1992 Caselli et al.
5,625,106 A * 4/1997 Marks et al. ............ 585/512
6,214,953 B1 4/2001 Oh et al.
6,360,983 B1 * 10/2001 Sikorski, Jr. ............ 526/39
8,071,885 B2 * 12/2011 Wu et al. ............... 585/823

FOREIGN PATENT DOCUMENTS

OTHER PUBLICATIONS

ABSTRACT
An approach that permits continuous batch conversion of alpha-olefins and internal-olefins to oligomeric materials without fouling the reaction vessel and provides a simple and highly efficient method for making very cost effective catalytic systems based on Ziegler-Natta Group 4 metalloenes. Embodiments of this invention produce diesel and turbine fuels that are 100% synthetic iso-paraffinic kerosenes with flashpoints greater than 61 deg C.

12 Claims, 1 Drawing Sheet
(56) References Cited

U.S. PATENT DOCUMENTS

2012/0238788 A1 9/2012 Wright et al.
2013/0032550 A1 2/2013 Wright et al.
2013/0197279 A1 8/2013 Wright et al.

FOREIGN PATENT DOCUMENTS

WO WO 2010/136289 A2 12/2010
WO PCT/US12/35126 4/2012
WO PCT/US12/35132 4/2012
WO PCT/US12/35167 4/2012


OTHER PUBLICATIONS


* cited by examiner
HOMOGENEOUS METALLOCENE ZIEGLER-NATT CATALYSTS FOR THE OLIGOMERIZATION OF OLEFINS IN ALIPHATIC-HYDROCARBON SOLVENTS

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part application, claiming the benefit of parent application Ser. No. 12/511,796 filed on Jul. 29, 2009, which is now U.S. Pat. No. 8,395,007 and parent application Ser. No. 12/550,973 filed on Aug. 31, 2009, which is now U.S. Pat. No. 8,227,651, and parent provisional application Ser. No. 61/585,943 filed Jan. 12, 2012, whereby the entire disclosures of which are incorporated hereby reference.

STATEMENT FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

The invention described herein may be manufactured and used by or for the government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

FIELD OF THE INVENTION

The invention generally relates to an approach that permits continuous batch conversion of alpha-olefin and internal olefins to oligomeric materials without fouling the reaction vessel and provides a simple and highly efficient method for making very cost effective catalyst systems based on Group 4 metalloccenes. Embodiments of the invention create synthetic isoparaffinic kerosenes with high flashpoints suitable for use gas, diesel, and turbine engines.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a photograph of a beaker removed directly from SS-bomb showing a typical homogeneous oligomeric mixture from 1-butene that contains the Cp₂ZrCl₂/MAO catalyst system prepared in cyclohexane, according to embodiments of the invention.

It is to be understood that the foregoing general description and the following detailed description are exemplary and explanatory only and are not to be viewed as being restrictive of the invention, as claimed. Further advantages of this invention will be apparent after a review of the following detailed description of the disclosed embodiments, which are illustrated schematically in the accompanying drawings and in the appended claims.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

The invention generally relates to an approach that permits continuous batch conversion of alpha-olefin and internal-olefinsto oligomeric materials without fouling the reaction vessel and provides a simple and highly efficient method for making very cost effective catalyst systems based on Group 4 metalloccenes.

Most homogeneous ZN catalyst are prepared in aromatic solvents. This invention provides a versatile and inexpensive means for creating and using highly active catalysts for the oligomerization of alpha-olefins, like 1-butene. Hence, very valuable for turning 1-butene (made from bio-1-butanol) to oligomers suitable for use in creating diesel and jet fuels with flashpoints over 61 deg C. Furthermore, by addition of a homogeneous isomerization catalyst mixtures of alpha-olefins and internal-olefins can be converted to high flashpoint diesel and jet fuels using highly active homogeneous ZN invented herein.

An aspect of the invention includes a fuel(s) produced from oligomerization and/or dimerization processes including; at least one alpha-olefin and/or internal olefins, at least one homogeneous Ziegler-Natta catalyst, at least one homogeneous activating co-catalyst, and at least one mixture hydrocarbon solvent, where the fuel has a flashpoint of 61 to 100° C. Embodiments of the invention further include at least one olefin-isomerization catalyst. Other embodiments of the invention include a Ziegler-Natta catalyst having group four (4) metalloccene catalyst. In other embodiments, the co-catalyst is an alkylaluminumoxane (AAO). Yet in other embodiments, the catalyst is prepared by contacting a metalloccene precatalyst with an aliphatic hydrocarbon solution having an alkylaluminumoxane (AAO). In still yet other embodiments, the aliphatic hydrocarbon solution is derived from a fuel.

Embodiments of the invention include the catalyst being prepared by dissolving trialkylalane in an aliphatic-hydrocarbon solvent and/or fuel and treated with one mol-equivalent of water and are then contacted with a metalloccene precatalyst and filtered. In embodiments, the trialkylalanes are selected from the group consisting of trimethylalane, triethylalane, tributylalane, and tri(iso-butyl)alane (TIBA). In other embodiments, the aliphatic hydrocarbon solvents and/or fuels are selected from the group consisting of straight chain alkanes including hexanes, heptanes, octanes, nonanes, decanes, and alkanes having greater than 10 carbons. In yet other embodiments, the aliphatic hydrocarbon solvents and/or fuels are selected from the group consisting of, but not limited to, branched-aliphatic hydrocarbons including 3-methylheptane, 2-methyloctane, and 6 to 16 carbons. Still yet in other embodiments, the aliphatic hydrocarbon solvents and/or fuels are selected from the group consisting of, but not limited to, cyclic aliphatic-hydrocarbons including cyclohexanes, methycyclopentanes, dimethylcyclohexanes, tetralins, pinanes, and other mono- and bicyclic aliphatic-hydrocarbons.

Another aspect of the invention includes a process for preparing a saturated hydrocarbon solution/fuel including; an Activated Homogeneous Metalloccene Catalyst (AHMC) for use in the dimerization and oligomerization of neat α-olefins, where AHMC is prepared by contacting a metalloccene precatalyst of the formula (I) with an alkylaluminoxane of formula (II), where the latter is prepared in a saturated hydrocarbon solution/fuel:

\[ L^{1+} \cdot MX^2 \]  

(II)

where: M is Ti, Zr, or Hf, X¹ and X² is at least one halogen, hydrogen, alkyl, or a mixture thereof, L¹ and L² are comprised of π-ligands selected from the group consisting of cyclopentadienyl, indenyl, fluorenyl and derivatives thereof, where substituents are attached to the ligands, the attachments includes ansa-linkages that bind the two rings, with at least one carbon or silicon atoms each bearing hydrogen or alkyl radicals, at least one saturated hydrocarbon solvent/fuel.
selected from the group consisting of cycloalkanes, normal-
alkanes, and/or iso-alkanes, n is an integer of at least 3, and R
is a C₃₋C₃₀ alkyl, linear, branched, or combination thereof.
Embodiments of the invention include the AI/M molar ratio
being about 1 to 100. In other embodiments, the AI/M molar
ratio is 10 to 20. Embodiments of the invention include the
AHMC being prepared by placing in contact with a neat
solution having at least one α-olefin during a period of 1 to 24
h and forms the α-olefinic-oligomer (III) in 98-100% conver-
sion based on starting α-olefins:

![Diagram](image)

Embodiments of the invention include the AHMC being
introduced in one portion, in discrete aliquots, or through a
continual addition process directly to the neat α-olefins.
Embodiments of the invention include the ratio of metal-
locene catalyst (g of M) to α-olefinic-oligomer product
(Kg) is about 5 to 40. In other embodiments, the entire
α-olefinic-oligomer product (III) is transferred to a quench
vessel, treated with water, and then filtered to remove solids.
In other embodiments, the α-olefinic-oligomer product (III)
is passed through an alumina or another metal oxide filter
material to remove M and AI species from the product solution.
Other embodiments, the α-olefinic-oligomer product (III) is
treated with a stabilizing agent selected from either a hydro-
quinoine or phenol family of stabilizers, with butylated
hydroxyl toluene (BHT) and at concentrations of 10-300
ppm.

Embodiments of the invention include the process lower-
ing the boiling fraction of the α-olefinic-oligomer products
(III) between 50°C and 150°C, including between 70°C and
130°C, and are removed by flash distillation. Embodi-
ments of the invention include the process having a low
boiling fraction from about 25 to 45 wt-% of the total α-olefinic-
oligomer product, or comprises about 30-40 wt-% of the total
α-olefinic-oligomer. In embodiments, the process includes
a light boiling fraction subjected to selective-racemization
chemistries to create a mixture of mono-olefinic hydrocarbon
products having a boiling point greater than 200°C but less
than 300°C at atmospheric pressure. Embodiments of the
invention include the process having a high boiling fraction
subjected to catalytic hydrogenation over heterogeneous
metal catalysts having palladium, platinum, and/or nickel (or
any combination thereof). Embodiments of the invention
include the process having a hydrogen pressure in the range
of about 30-3000 psig, or a pressure between 50 and 100 psig.
Embodiments of the invention the reaction temperature used
is in the range of about 20 to 100°C with ambient or 40°C
temperature range.

Embodiments of the invention further include the product
being subjected to hydrogenation over heterogeneous metal
catalysts which includes palladium, platinum, and/or nickel;
hydrogen pressure is performed in the range of about 30-3000
psig, or a pressure between 1000 and 2000 psig. In embodi-
ments, the temperature is in the range of 20 to 100°C or 60°C
to 80°C temperature range. In embodiments, the products
are combined and distilled at atmospheric pressure. In other
embodiments, the products obtained are combined and dis-
tilled at reduced pressure. Embodiments of the invention a
collection of hydrocarbon, a completely 100% synthetic iso-
paraffinic kerosene (SiPK) product, starting at 150°C and
finishing at 280°C affords a fuel mixture that meets Jet-A/
JP-8 and diesel #1 flashpoint requirements (≥38°C). Embodi-
ments of the invention the SiPK jet/diesel fuel produced
has a derived Cetane index of 40-55 or 50 Cetane index.
In other embodiments, the SiPK jet/diesel fuel produced has a
maximum cold flow viscosity of 8 cSt as measured at −20°C.
(ASTM 445L)

Embodiments of the invention include the collection of
product starting at 170°C and finishing at 280°C yields a
SiPK jet/diesel that meets military JP-5 and diesel #2 flash-
point requirements with a flashpoint >61°C. Embodiments of
the invention include the SiPK jet/diesel fuel produced has a
derived Cetane index of 40-55 or 50 Cetane index. Embodi-
ments of the invention include SiPK jet/diesel fuel produced
has a maximum cold flow viscosity of 8.5 cSt as measured at
−20°C. (ASTM 445L). Embodiments of the invention include
the α-olefins are selected from the group consisting of,
but not limited to, 1-propane, 1-butene, 1-pentene, and
1-hexene, with neat 1-butene or a mixture of 1-butene and
1-propane (3:1, mol:mol, respectively).

Embodiments of the invention include the π-ligands being
cyclopentadienyl, R is methyl, and the aliphatic hydrocarbon
solution/fuel is cyclohexane or methylcyclohexane. Embodi-
ments of the invention include the π-ligands are cyclopa-
entadienyl rings having at least one alkyl group attached. R
is methyl, and the aliphatic hydrocarbon solution/fuel is
selected from the group consisting of cyclic, acyclic linear
and branched hydrocarbon solvent that include jet and diesel
fuels prepared. Embodiments of the invention include the
π-ligands being cyclopentadienyl, R is at least three carbons,
and the aliphatic hydrocarbon solution/fuel is selected from
acyclic linear and/branched hydrocarbon solution/fuel.

Embodiments of the invention include the trialkylalane
compound being prepared by direct reaction of one mol of
trialkylalane with an mol-equivalent of water in the SiPK.
Other embodiments of the invention include the trialkylalane
is selected from the group consisting of, but not limited to,
trimethyl, triethylalane, tripropylalane, tri-isopropylalane,
tributylalane, and tri-isobutylalane, and tri-isobutylalane. In
other embodiments, the trialkylalane compound is prepared
by direct reaction of one mol of trialkylalane with an mol-
equivalent of water in the SiPK. Yet in other embodiments,
the trialkylalane is selected from the group consisting of,
but not limited to, trimethyl, triethylalane, tripropylalane, tri-isoprop-
ylalane, tributylalane, and tri-isobutylalane, and tri-isobutyl-
alane. Still yet in other embodiments the π-ligands are cyclo-
pentadienyl rings having at least two alkyl groups attached, R
is methyl, and the aliphatic hydrocarbon solution/fuel is
selected from the group consisting of cyclic, acyclic linear,
branched hydrocarbon solvent, and jet and diesel fuels pre-
pared. Embodiments of the invention include a fuel having a
flashpoint of about 61 to about 100. Embodiments of the
invention further include an isomerization catalyst having a
range from about 0.1 ppm to about 0.1 weight%, relative to
the total olefin component.

Oligomers, suitable for conversion and use as jet and diesel
fuels, are prepared from α-olefins using highly active
purely homogeneous Ziegler-Natta catalysts, a homogeneous
catalyst, and in pure aliphatic hydrocarbon solvent. The
oligomerization can be conducted controlled without the use
of hydrogen and produce an ideal molecular distribution of
oligomers for use in preparing diesel and jet fuels. This
method creates fuels that do not require any subsequent
hydrocracking or reforming yet retain outstanding cold flow
properties and exceptionally high gravimetric densities.
The homogeneous catalyst of embodiments of the invention is prepared by contacting a metallocene precatalyst with a solution of an alkylaluminoxane (AAO). Typically, R¹ and R² can be hydrogen or any combination of C₁-C₃₀ alkyl chains. The R¹ and R² substituents(s) are linear or branched chains and/or a combination thereof. The alkylaluminoxane can be prepared using methods that familiar to those in the art and R² is a C₁-C₃₀ alkyl group, although larger chains can be employed. Branching in the alkyl group can be used to increase solubility although it is not required in this invention. When the AAO is prepared in an aromatic solvent, the metallocene precatalyst is combined and the aromatic solvent is removed under reduced pressure and the solids redissolved in the desired aliphatic-hydrocarbon solvent or fuel, filtered if necessary, and then transferred to the reaction vessel that contains the mixture of alpha-olefin and internal-olefins. These activated homogeneous catalyst solutions are stably and suitable for storage. Typical alpha-olefins would include R¹ being a C₁-C₁₀ alkyl group that can be a linear chain or contain branching at various places in the carbon chain. The internal olefin is any olefin-isomer where the double bond has chemically migrated internally along the carbon chain. The homogeneous isomerization catalyst takes the internal-olefin and isomerizes the bond so as to create the corresponding alpha-olefin.

Another embodiment of the chemical process for preparing the homogeneous metallocene catalyst in pure aliphatic-hydrocarbon solvent follows:

Atrialkyllane is dissolved in an aliphatic-hydrocarbon solvent and treated with one mol-equivalent of water, this solution is then placed in contact with a metallocene pre-catalyst. The molar ratio of alkane/metallocene can be varied from 1:1 to 100:1, respectively, depending on the desired catalytic process and outcome. The final solutions may be filtered to remove any impurities or undesired products resulting from the controlled hydrolysis of the alkane and subsequent reaction with the metallocene pre-catalyst. The liquid solutions are typically light yellow in color and crystal clear to the eye. Typical concentrations of the active homogeneous catalysts are around 0.01M to 0.05M, with lower concentrations being possible with equal catalytic activity. These latter solutions can be stored for long periods or immediately transferred to reaction vessels using common techniques that include Teflon® diaphragm pumps or by simple polypropylene syringes, all with equal success and retention of catalyst activity.

Typical aliphatic-hydrocarbon solvents useful in this invention include straight chain alkanes such as hexane, heptanes, octane, nonane, and decane. Branched-aliphatic-hydrocarbons such as 3-methylheptane, 2-methylheptane, and 2-methylcyclooctane work well in this invention as well as other branched aliphatic hydrocarbons containing from 6 to 16 carbons. In particular, the use of C₁₂ to C₁₆ saturated synthetic iso-paraffinic kerosenes are for use in this embodiment. Cyclic aliphatic-hydrocarbons can be used that include cyclo-hexane, methylcyclohexane, dimethylcyclohexanes, tetralin, pinane, and other mono- and bicyclic aliphatic-hydrocarbons.

Useful metallocene pre-catalysts for this invention can be prepared by several methods, some found in the open literature covering nearly four decades of group metallocene syn-
Oligomerization of an Alpha-Olefin Using a Homogeneous Zn-Catalyst Delivered in an Aliphatic Hydrocarbon-Solvent.

1-Butene (~390 g, ~500 mL, CP grade) was condensed over calcium hydride inside a Schlenk flask maintained at ~70° C, and re-evaporated and passed through a column of activated alumina in route to being condensed inside a dried 0.7 L capacity PARR SS bomb. A 500 mL beaker was placed inside the bomb to simulate a glass lined reaction vessel. Once the 1-butene was condensed inside the SS bomb the sample was subjected to five evacuation/backfill cycles to remove residual amounts of oxygen. The homogeneous aliphatic-hydrocarbon solution containing the active catalyst was added to the mixture and 3 addition evacuation/backfill cycles were performed. The SS bomb was sealed and allowed to react for 8 h. Shorter times could be used if the SS bomb was warmed by external heat. Typically after ~1 h the bomb reached a maximum pressure of 80 psig and approached 60° C, in temperature. At completion of the reaction little or no pressure remained in the vessel and the when removed from the SS bomb the beaker contained a clear light yellow solution of oligomers (see FIG. 1). Quenching the mixture with 0.5 mL of water and then drying over potassium carbonate (~3 g) afforded ~380 g of an oligomeric mixture suitable for use in making diesel and jet fuels with flash points over 61 deg C.

FIG. 1. Beaker removed directly from SS-bomb showing a typical homogeneous oligomeric mixture from 1-butene that contains the Cp2ZrCl2/MAO catalyst system prepared in cyclohexane. Sample contains no aromatic-hydrocarbons.

The following examples are for illustration purposes only and not to be used to limit any of the embodiments.

EXAMPLE 1

Preparation of the Homogeneous Zn-Catalyst in an Aliphatic-Hydrocarbon Solvent.

A Schlenk flask was charged with Cp2ZrCl2 (0.080 g, 0.274 mmol) and 10 mL of a toluene MAO solution (8.0 wt% active MAO). The toluene was removed under reduced pressure to afford a yellow solid. To this mixture was added cyclohexane (15 mL) and heated briefly with stirring to dissolve the activated catalyst. The solution was allowed to settle and clear yellow solution was collected by syringe (~10 mL) and used directly or stored for future use.

What is claimed is:

1. A fuel produced from oligomerization and/or dimerization processes, comprising:
   providing at least one alpha-olefin and/or internal olefins; adding at least one homogeneous Ziegler-Natta catalyst; adding at least one homogeneous activating co-catalyst; and
   adding at least one or mixture hydrocarbon solvent, wherein said fuel having a flashpoint of 61 to 100° C.
2. The fuel according to claim 1, further comprising at least one olefin-isomerization catalyst.

3. The fuel according to claim 1, wherein said Ziegler-Natta catalyst includes group four (4) metalloocene catalyst.

4. The fuel according to claim 1, wherein said co-catalyst is an alkylaluminoxane (AAO).

5. The fuels according to claim 1, wherein said catalyst is prepared by contacting a metalloocene precatalyst with an aliphatic hydrocarbon solution having an alkylaluminoxane (AAO).

6. The fuel according to claim 5, wherein said aliphatic hydrocarbon solution is derived from a fuel.

7. The fuels according to claim 6, wherein catalyst is prepared by dissolving trialkylalane in an aliphatic-hydrocarbon solvent and/or fuel and treated with one mol-equivalent of water and is then contacted with a metalloocene precatalyst and filtered.

8. The fuels according to claim 7, wherein said trialkylalanes are selected from the group consisting of trimethylalane, triethylalane, tributylalane, and tri(iso-butyl)alane (TIBA).

9. The fuels according to claim 6, wherein said aliphatic hydrocarbon solvents and/or fuels are selected from the group consisting of straight chain alkanes including hexanes, heptanes, octanes, nonanes, decanes, and alkanes having greater than 10 carbons.

10. The fuel according to claim 6, wherein said aliphatic hydrocarbon solvents and/or fuels are selected from the group consisting of branched-aliphatic-hydrocarbons including 3-methylheptane, 2-methyloctane, and 6 to 16 carbons.

11. The fuels according to claim 6, wherein said aliphatic hydrocarbon solvents and/or fuels are selected from the group consisting of cyclic aliphatic-hydrocarbons including cyclohexane, methylecyclohexanes, dimethylecyclohexanes, tetralins, pinanes, and other mono- and bicyclic aliphatic hydrocarbons.

12. A fuel produced from oligomerization and/or dimerization processes, comprising:
  providing at least one alpha-olefin and/or internal olefins; 
  adding at least one homogenous Ziegler-Natta catalyst; and
  adding at least one homogenous activating co-catalyst, wherein said fuel having a flashpoint 61 to 100°C.

* * * * *